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14. ABSTRACT Recent advances in the development of highly conductive ionic liquids have made them of interest for use as propellant in spacecraft propulsion systems. Electrospray thrusters apply strong electrostatic fields to an ionic liquid in order to extract and accelerate charged particles/droplets, producing thrust. The behavior of these ionic liquids as they pass through the components of an electrospray system can have a significant effect on thruster operation. The wetting and adhesion behavior between the ionic liquid propellant and solid materials can be characterized using the surface tension and contact or "wetting" angle formed when a liquid droplet comes in contact with a solid surface. Ideally this angle is a function of the interactions between the solids surface energy, the surface tension of the liquid and the interactions of both with the surrounding medium. Deviation from ideal contact angle behavior can indicate surface inconsistencies, environmental effects or contamination of the solid and liquid. Contact angle and surface tension measurements are presented for the ionic liquid propellant 1-Ethyl-3-methylimidazolium bis(triuoromethylsulfonyl)imide, called EMIIIm or EtMeImTf ₂ N, with respect to various substrate materials and environmental conditions. Analysis of these measurements determines optimum materials and operating conditions for current and future electrospray thruster designs.					
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Wetting Properties of EMIIIm & its Relevance to Electrospray Design

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Recent advances in the development of highly conductive ionic liquids have made them of interest for use as propellant in spacecraft propulsion systems. Electrospray thrusters apply strong electrostatic fields to an ionic liquid in order to extract and accelerate charged particles/droplets, producing thrust. The behavior of these ionic liquids as they pass through the components of an electrospray system can have a significant effect on thruster operation. The wetting and adhesion behavior between the ionic liquid propellant and solid materials can be characterized using the surface tension and contact or “wetting” angle formed when a liquid droplet comes in contact with a solid surface. Ideally this angle is a function of the interactions between the solids surface energy, the surface tension of the liquid and the interactions of both with the surrounding medium. Deviation from ideal contact angle behavior can indicate surface inconsistencies, environmental effects or contamination of the solid and liquid. Contact angle and surface tension measurements are presented for the ionic liquid propellant 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, called EMIIIm or EtMeImTf₂N, with respect to various substrate materials and environmental conditions. Analysis of these measurements determines optimum materials and operating conditions for current and future electrospray thruster designs.

Nomenclature

d	Distance between tip of Taylor cone and grid
D	Base diameter of a sessile droplet
H	Contact angle hysteresis
K	Coefficient used in Eotvos model
k	Coefficient describing dynamic angle behavior
n	Coefficient describing dynamic angle behavior
R_a	Surface roughness averaged over a 1D profile
r_s	Ratio of actual to apparent surface area
S	Distance separating two grid apertures
T	Absolute temperature of the test liquid
T_C	Critical temperature of the test liquid
V	Molar volume of the test liquid
γ_l	Surface tension of the fluid
γ_s	Surface free energy or critical energy of the solid
γ_{sl}	Surface energy between the liquid and solid
π_{sl}	Adhesion tension between the liquid and solid
θ	Idealized contact angle from Young’s Equation
θ_A	Contact angle as droplet base advances
θ_M	Effective angle due to chemical reaction
θ_R	Contact angle as droplet base recedes
θ_W	Effective angle due to surface roughness

Introduction

The significance of propellant wetting behavior with respect to electrospray operation has been described by multiple researchers.^{1,2,3,4,5} It has been shown that

component/propellant wetting affects Taylor cone formation, the propellant feed system and overall reliability of electrosprays. Several methods have been developed to either inhibit or promote wetting between ionic liquid propellants and various solid electrospray components. These methods include the choice of solid materials being used as insulators, emitters or electrodes, thin film surface coatings that have a desired high or low wettability, and changing the solid component surface roughness or temperature during operation.^{6,7,8}

An electrospray thruster has been developed by North American Space Agency (NASA) Jet Propulsion Laboratory (JPL), and is scheduled to launch in April of 2012 on the Laser Interferometer Space Antenna (LISA) Pathfinder spacecraft as part of the Disturbance Reduction System (DRS) payload.^{9,10} Lisa Pathfinder is part of the European Space Agency’s (ESA) Small Missions for Advanced Research in Technology (SMART) program. Two electrospray clusters will be used as a technology demonstration, providing propulsion to counteract drag effects on the spacecraft.⁹ The design uses an internally wetted emitter and the ionic liquid propellant 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, called EMIIIm.⁵ During research and development of this system it was concluded by Conroy and Ziemer et. al. that the wetting characteristics of EMIIIm in contact with solid emitter materials can have an effect

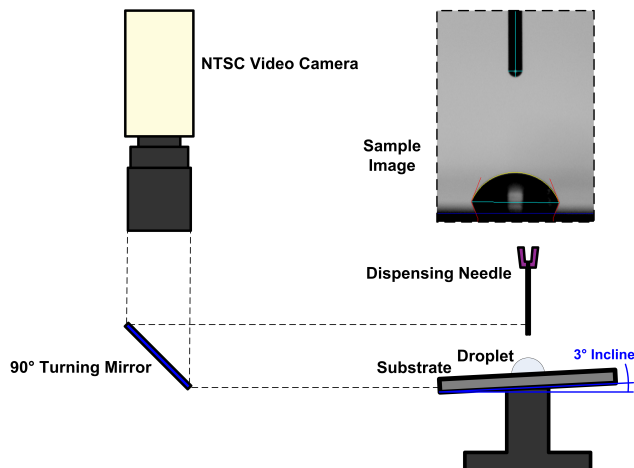
on thruster performance and reliability.⁵ The need for additional data on wetting angles for EMIIIm in combination with different materials suitable for electrospray use was specifically cited.

Due to their recent development many of the properties of specific ionic liquids such as EMIIIm and their interactions with different solid materials are unknown. The liquid surface tension of EMIIIm is well characterized however its wetting behavior in contact with different solid materials is not. The following research presents measurements and analysis of EMIIIm wetting properties when in contact with different solids, varying surface roughnesses, and under different operating conditions. Wetting properties are characterized by contact angle measurements taken using the goniometer-sessile drop technique. We also examine the surface tension of the liquid for comparison using the pendant drop method. Measurements are taken with EMIIIm and different solid substrates typically used to form electrospray emitters and extraction/acceleration grids. This research will provide insight as to the ideal conditions and suitable materials for optimal electrospray thruster design.

Testing Facilities

Measurements were performed in Chamber 8 at the Air Force Research Laboratory, Edwards Air Force Base California, spacecraft propulsion directorate. Chamber 8 is a bell jar vacuum chamber capable of 10^{-6} Torr pressures with an interior working volume of 80 liters. Vacuum was achieved using a two stage system, the first stage being a Varian Triscroll 600 oil-less pump. Minimum first stage pressures were on the order of 10^{-3} Torr. The second stage was a Varian TV301 turbopump with a Varian V-301 turbopump controller. Pressure measurements were provided using two MKS pirani gauges and an MKS Series 943 cold cathode gauge. Pressure inputs were digitized by an MKS 937A pressure gauge controller and recorded using National Instruments LabVIEW 7.

Measurements were made using a First Ten Angstroms model 125 surface tension and contact angle instrument shown below in Figure 1.¹¹ The FTA125 consists of an analog NTSC camera for capturing video or still images. The camera is oriented to view the syringe needle tip/droplet profile and substrate via a 90° turning mirror. The camera is mounted vertically while the droplet and substrate are oriented 3° off horizontal (inclined towards the mirror), below the camera. The slight incline allows full view of the droplet profile and base as it rests on the substrate. This imaging system is illustrated in Figure 1. The FTA125 provides for real time video monitoring and recording as the liquid forms a “pendant drop” at the syringe tip and after the droplet has been deposited on the substrate surface. FTA32 software included with the FTA125 ran on a Microsoft Windows[®] PC



a) Diagram of FTA125 imaging method.



b) Picture of standard FTA125 instrument, unmodified.

Fig. 1 FTA125 setup and orientation.

and provided video drop shape analysis, allowing both static and time resolved measurements of surface tension, contact angle, droplet volume, base diameter and several other measurements. The FTA125 was calibrated using a sapphire spherical lens standard, 6mm in diameter, embedded in an aluminum carrier block forming a $90^\circ \pm 1^\circ$ angle, also purchased from FTA.

Several modifications were made in order to operate the system remotely, in a vacuum chamber, and allow temperature control and feedback. These modifications allowed multiple test droplets to be dispensed on fresh substrate without re-pressurizing from vacuum. This was accomplished using a remotely actuated servo motor driven stage, to move the substrate

sample back and forth, exposing new substrate material. Multiple droplets could then be dispensed, maximizing the number of measurements possible without re-pressurizing. A stepper motor driven plunger allowed remotely controlled dispensing of fluid at a consistent flow rate.

Thermal controls were added in order to vary the temperature of the solid substrate, test fluid and ambient air (when testing in atmosphere). Substrates were mounted on a copper plate brazed with copper tubing that could be heated or cooled using a PolyScience, 6 Liter reservoir, re-circulating fluid bath system capable of temperature ranges between -20 and 150° Celsius. The heating and cooling fluid used was ethylene glycol. The bath was also used to heat and cool the custom machined stainless steel reservoir that the EMIIIm passed through before being dispensed. This allowed control of the fluid temperature immediately before coming to the end of the needle tip. The internal air temperature of the vacuum chamber was controlled during atmospheric pressure testing using an incandescent 360 watt projector lamp heating an aluminum radiator. Internal chamber air was circulated over the radiator using an 80mm fan. The fan was disengaged during measurements to reduce droplet perturbations due to turbulent air flow in the chamber. With this system it was possible to heat the internal air temperature of the chamber to 70° Celsius, though at this temperature the FTA125 camera electronics began to show signs of overheating.

Temperature measurements were made using five Omega K-type thermocouples. Temperatures were measured at the following locations: substrate surface, copper cooling/heating plate interior, stainless steel fluid channel interior, fluid reservoir exterior and in ambient air/vacuum. The location of each of these measurements are illustrated in Figure 2. Thermocouple signals were digitized using a National Instruments Fieldpoint bank (FP-1601 & FP-TC-120) and recorded to file using LabVIEW 7.

EMIIIm & Substrates

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIIIm, CAS# 174899-82-2), is a room temperature ionic liquid, $[C_6H_{11}N_2]^+[N(SO_2CF_3)_2]^-$. EMIIIm has several properties that make it suitable as an electrospray propellant. These properties include a relatively low viscosity, high conductivity, negligible vapor pressure and a large charge to mass ratio.⁵ The EMIIIm obtained for this research was purchased from Strem Chemicals Inc., Newburyport, MA 01950. The EMIIIm came in capped, wax sealed bottles packed with dry nitrogen. Measurements using Karl-Fisher titration showed that the EMIIIm, taken from a factory sealed bottle, immediately after opening, contained 2411 ± 41 ppm water by mass fraction. Waste EMIIIm

Table 1 EMIIIm Properties (at 1 atm, 20 °C)

Property	Value	Units
Density ¹⁵	1523.6	kgm^{-3}
Vapor Pressure ⁵¹²	Negligible	
Surface Tension*	38.1	Jm^{-2}
Expansion Coefficient ¹³	6.47×10^{-4}	K^{-1}
Critical Temperature ¹²	1123	K

* Value measured during this research

Table 2 List of materials tested.

Material	Thickness[mm]	Ra [μm]
Fused Silica	0.5	<0.144
Soda Lime Glass	1	<0.144
Kapton	0.05	0.144
PTFE Teflon	1.38	1.47
Pyrex	1	<0.144
Annealed Titanium	13	0.600
Unsintered Tungsten	1	0.351
Undoped Silicon	0.5	<0.144
Stainless Steel 316	4.7	0.634/1.20/2.52

used for this experiment and exposed to ambient atmosphere for several months was measured as having a water content of 2825 ± 16 ppm by mass fraction. Water content has been discussed as a source of uncertainty in surface science measurements.¹²¹³¹⁴ Some relevant properties with respect to surface science are listed in Table 1.

Eleven materials suitable for use in different electrospray components were obtained to test with. Three of these substrates were the same material (stainless steel 316) each with a different surface roughness ranging from mirror polish to sandblasted with coarse grit. Each material, its thickness and measured surface roughness value R_a are listed in Table 2. Before each measurement a cleaning regimen was performed to mitigate contamination. The first step involved placing the substrate in a clean Pyrex petri dish and cleaning the surface with acetone and Kimberly-Clark® Kimwipes EX-L. The substrate was then rinsed with demineralized water and heated to approximately 120° Celsius for 20 minutes to vaporize any remaining water. The petri dish was then covered, and allowed to cool to ambient temperature.

Contact Angle Theory

Young's Equation

The relationship between contact angles and the surface tension/energy components of a three phase wetting system were originally described by Thomas Young in the 1800's. It was recognized that the idealized contact angle θ is a function of the balance between three surface energy terms, each of which are primarily driven by van der Waal's forces. These energy terms are; γ_l , the surface tension of the liquid phase (the sessile droplet); γ_s , the surface free energy of the solid substrate (sometimes equated to the critical surface energy); and γ_{sl} , the surface interfacial

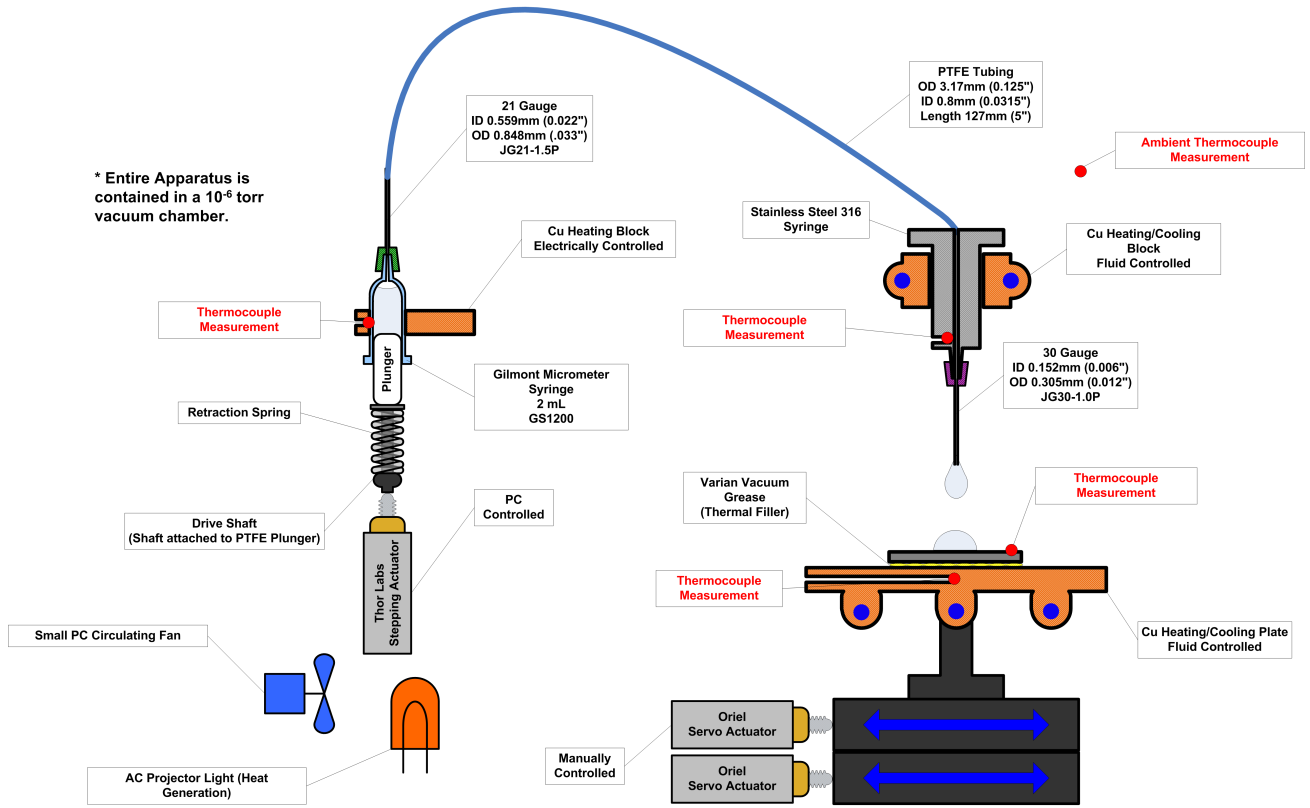


Fig. 2 Experimental setup with prominent features labeled.

energy between the liquid droplet and solid. Definitions for these terms are complex, but it suffices to think of them as the amount of reversible work required to form a unit area of free surface or interfacial surface. Young's Equation quantifying this relationship is shown in Equation 1, where the term π_{sl} is referred to as the adhesion tension and is (in most cases) equal to $\gamma_s - \gamma_{sl}$.¹⁶

$$\cos \theta = \frac{\pi_{sl}}{\gamma_l} \quad (1)$$

We can see from Equation 1 that if the surface tension of the liquid γ_l is relatively high compared to the adhesion tension, the contact angle will increase as the droplet's cohesive internal forces cause it to contract. If π_{sl} is significantly greater, the adhesive forces between the liquid and solid will cause the droplet to spread out and lower the contact angle. In this idealized system, we see that wetting is a function of the relative energies of adhesion tension and liquid surface

tension. The balance between these forces determine how easily a liquid will wet a solid and are a function of the intrinsic properties of each component in the system.

Hysteresis & Advancing-Receding Contact Angles

Advancing and receding contact angles are typically measured using the captive drop technique.¹⁶ In this method the dispensing needle tip is positioned close to the substrate such that it will be present inside the forming droplet. The test liquid is continuously pumped out at an extremely low flow rate, causing the three phase interaction boundary to constantly advance. The advancing contact angle θ_A will typically reach a stable value as the sessile droplet expands. To measure the receding angle θ_R the liquid is retracted back into the needle and the resulting angle measured as the liquid contracts. This method and its results are demonstrated in Figure 3.

It has been commonly observed that the contact

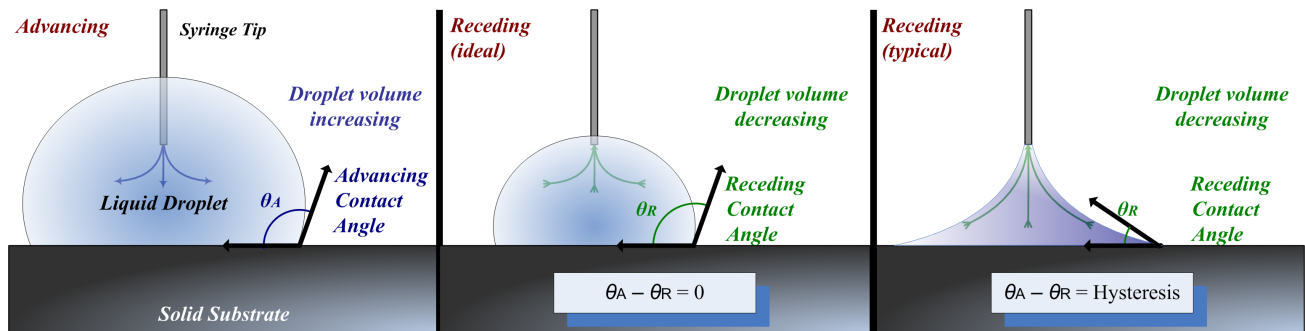


Fig. 3 Demonstration of the captive sessile droplet technique.

angle of a liquid advancing across a solid surface is different than the contact angle of the same fluid receding from the surface. In an ideal system, the contact angle is stable regardless of perturbations and both the θ_A and θ_R should be equivalent. The difference ($H = \theta_A - \theta_R$) between the two is defined as the contact angle hysteresis H . Hysteresis is due to surface heterogeneity such as surface roughness or porosity, impurities in the liquid or solid causing uneven surface or interfacial energies, swelling of the solid by the liquid, or a chemical reaction. Most researchers publish advancing contact angles as an approximation of the ideal contact angle previously described.¹⁷ Receding contact angles are also sometimes published to indicate the magnitude of these non-ideal interactions. Quite often the receding angle can be zero as the retracting liquid adheres to the solid surface and deforms from a bubble/droplet shape. In this case the base diameter remains relatively constant as droplet volume decreases. This is due to an effectively high π_{sl} caused by adsorption that is not part of the idealized contact angle theory described above.

Surface Roughness

Surface roughness is possibly the greatest source of uncertainty for contact angle measurements. The complexities due to the random nature of surface roughness on a microscopic level make modeling and analysis of its effects extremely difficult. The three phase boundary may be physically impeded from expanding, forming a force imbalance between the liquid surface tension and interfacial energies. In addition, impurities and small bubbles of the initial surrounding gas may become trapped in small scratches or depressions as the solid is wetted. In response to this uncertainty, many researchers publish surface roughness values for their test solids. A generalized expression to describe the effects of surface roughness was developed by Robert Wenzel in the early 1900's describing an "apparent" contact angle θ_W due to surface roughness which is a function of the idealized contact angle and the ratio, r_s , of the true surface area of the solid to the apparent area.¹⁸¹⁹ This expression is defined in Equation 2. The net result of surface roughness is that for liquid/solid wetting were the liquid surface energy

is the dominant term ($\theta > 90^\circ$), the effective contact angle due to roughness will be greater ($\theta_W > \theta$).¹⁹ The reverse is true for systems where the adhesion tension is the greater term ($\theta < 90^\circ$), the surface roughness will induce more wetting than an equivalent smooth solid ($\theta_W < \theta$).¹⁹ This latter case is more common as most liquid and solid materials will form a contact angle less than 90° .

$$\cos \theta_W = r_s \cos \theta \quad (2)$$

Chemical Reactions

Under ideal conditions we assume the components of our wetting system to be chemically stable and inert. In reality this is not always the case, even though the typical signs of a reaction (heat, light, gas generation) may be too small to measure, chemical reactions are known to affect contact angle measurements. This behavior is exhibited as a dynamic contact angle with respect to time.¹⁷¹⁶ The droplet will slowly spread or contract, causing the contact angle to "wander" to a lower value. Though this behavior is an uncertainty in contact angle analysis, it can serve as a useful indicator of material interactions. If all three components are shown to be an inert combination, dynamic behavior of the contact angle can indicate a contaminant is present. A characteristic expression for the behavior of contact angles with respect to time, due to chemical reaction, was developed by Marmur et. al. A modified form is shown in Equation 3, where θ_M is the effective contact angle of the droplet, k and n are empirical coefficients and t is the time from the initial contact between the liquid droplet and the solid.²⁰ k can be thought of as the initial contact angle that decays over time t as the droplet spreads out at a rate determined by n .

$$\theta_M = kt^n \quad (3)$$

Eotvos Model for Surface Tension

If the temperature of a liquid/solid wetting system changes, the surface energies of the components will change and the contact angle is affected. This is primarily due to variation of the liquid surface tension with temperature. In order to evaluate this

effect a mathematical expression describing surface tension as a function of temperature was first developed by Lorand Eotvos. It is known as the Eotvos rule and is shown in Equation 4, where V is the molar volume of the liquid, K is a constant ($2.1 \times 10^{-7} J \cdot K^{-1} \cdot mol^{\frac{2}{3}}$), T is the temperature of the fluid and T_C is the critical temperature of the fluid.¹⁹

$$\gamma_{lv} V^{\frac{2}{3}} = K (T_C - T) \quad (4)$$

Effect of Contact Angle on Electrospays

Internally Wetted Emitters

Conroy and Ziemer studied the effect on electro-spray performance when contaminant water is present in EMIIIm propellant.⁵ The primary consequence of this is possible bubble formation in propellant feed lines upstream of the emitter tip. These bubbles, if unconstrained, can expand in a low vacuum environment, and have a negative effect on performance. It was shown that the way propellant meniscus forms at the tip of the emitter can change the pressure acting on the upstream propellant. If the resulting meniscus pressure due to propellant surface tension and droplet size is greater than the vapor pressure of the contaminants, bubble formation can be inhibited.⁵ It was concluded that the contact angle can be used to calculate the likelihood of bubble formation in the propellant lines flowing EMIIIm.

Porous & Externally Wetted Emitters

For externally wetted emitters propellant must flow to the emitter tip due to capillary action. Multiple researchers have stated the need for externally wetted and porous emitter materials to be easily wetted by propellant.⁶⁷⁸³ Silicon has been used in many electrospays as an externally wetted emitter material due to its properties as a semiconductor. Despite doping and surface treatments meant to improve wettability several researchers have pointed out silicon's poor wetting characteristics with most ionic liquids. This makes evaluating new emitter materials using contact angles and the rate of spreading very important, as propellant feed to the emitter is critical for reliability.

Grid Obstruction & Arcing

Another Problem affecting electro-spray performance has been arcing between the emitter and extraction grid as well as obstruction of grid apertures due to errant propellant.³⁸ Arcing has typically been due to the presence of excessive propellant at the emitter tip.¹ When electric fields are applied, the droplet of propellant at the tip forms a Taylor cone and, the larger the initial droplet, the longer the Taylor cone will be. If the Taylor cone is sufficiently long it may come in close enough proximity to arc with the grid and either dam-

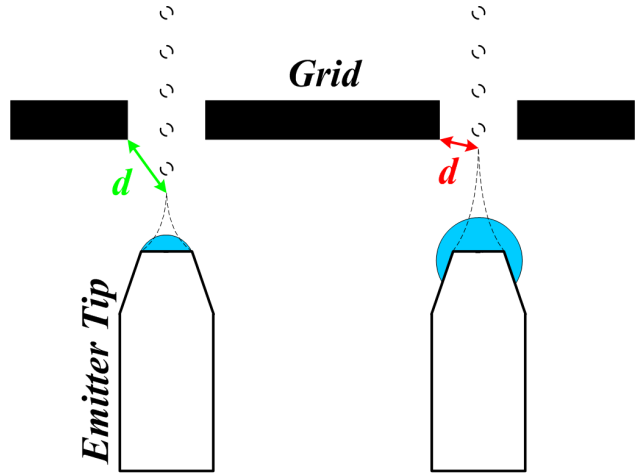


Fig. 4 Proximity of Taylor cone to the grid, as a consequence of droplet size i.e. contact angle.

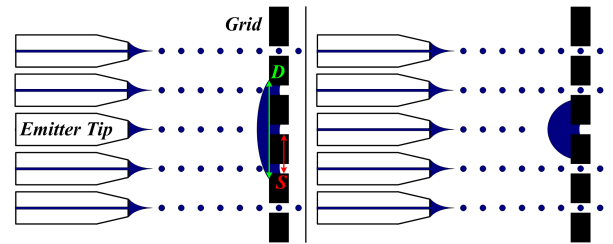


Fig. 5 Accumulation of propellant on emitter grid with low contact angle (left) & high contact angle (right).

age the emitter or short the high voltage circuit. This effect is shown in Figure 4 Conroy and Ziemer's work, mentioned previously, determined that the volume of propellant forming at the tip of the emitter can be affected by contact angle between the propellant and emitter material.⁵ For a larger contact angle, a larger volume of propellant will form at the emitter tip and the opposite is true for a smaller angle. This shows the contact angle's usefulness in identifying materials that may help reduce the likelihood of arcing between the emitter and extraction grid.

Another failure mechanism for electrospays is obstruction of the grid due to errant propellant. Occasionally the trajectory of an individual droplet of propellant will become skewed and it will accumulate on the grid instead of passing through. Over time multiple droplets can accumulate, forming an obstruction, effectively disabling one or more emitter/aperture pairs. Over time, if this accumulation has a high propensity for wetting, it could spread to block multiple apertures and adversely effect the overall electro-spray performance. This concept is shown in Figure 5. This implies that, in order to mitigate this problem, grid or grid coating materials should not be easily wetted by the propellant. This behavior would be evident as a higher contact angle due to less wetting and adhesion.

Results and Discussion

EMIIm Surface Tension

The surface tension γ_l of EMIIm was measured with respect to ambient conditions, beginning with temperature $\gamma_{lv}(T)$. These tests involved driving the internal ambient temperature of the chamber (at atmospheric pressure) to different values. Once the internal temperature of all the components had stabilized, EMIIm was then pumped through the dispense system at a slow flow rate until forming a pendant drop (typically $2\text{ }\mu\text{L}$ in volume) at the syringe tip. The pendant drop was then recorded and analyzed using the FTA125 and accompanying FTA32 software.

The resulting data and corresponding linear curve fits establishing EMIIm surface energy as a function of temperature are shown in Figure 6. Each data point taken (shown as orange circles) is an average of twenty separate pendant drop tests taken at the same temperature setting. Also shown in Figure 6 are the same measurements taken on EMIIm in previous work by other researchers using the same pendant drop technique, and the Wilhelmy Plate method.¹³¹²¹⁴ Data calculated using the Eotvos model from Equation 4 and published properties of EMIIm listed in Table 1 are also plotted. Data taken at AFRL agrees fairly closely with other researchers and the model, though relative inaccuracy in the measurement makes the temperature trend less clear. The observed inaccuracy may be due to water content, differences in sample handling or the details of taking measurements using the FTA125. This test showed that the EMIIm obtained for this experiment exhibited the same properties described in contemporary work and measured with similar methods.

Measurements were also taken to determine the effect of ambient pressure on EMIIm surface tension. Ideally this measurement would have involved forming a single pendant drop and then varying the pressure through an entire range from ambient to the lowest pressure possible. Unfortunately, changing the ambient pressure while a pendant drop was present at the tip of the dispense needle typically resulted in the drop being dislodged or retracted. This was due to vibration and air bubbles that would inevitably become trapped in the dispense system. When decreasing chamber pressure, the trapped air would expand and push more fluid out. When allowing chamber pressure to rise back to ambient the opposite would occur and the droplet would retract into the needle tip. In either case the measurement was negatively effected. To address this issue, pendant drops were formed and measured at a single pressure for each test. Only two pressures were measured, ambient atmosphere (1 ATM, 760 Torr) and the lowest pressure attainable by vacuum Chamber 8 (averaged over all tests, approximately $40\text{ }\mu\text{Torr}$). The resulting data is shown in Figure 7.

Each data point in Figure 7 is an average of eight measurements. The results showed no noticeable change in surface tension between the two pressures. This indicated that any change occurring in EMIIm surface tension due to changing pressure was too small to measure with this apparatus. Additional measurements were then taken where temperature was varied in a similar fashion as the previous test, to see if pressure change would have an effect on the temperature trend. Note that measurements taken at ambient pressure were limited to a maximum temperature of approximately 50K . Above this temperature the ambient air would transfer enough heat to the enclosed camera to affect its operation. There remained no clear relationship between EMIIm surface tension and ambient pressure. This is likely due to EMIIm's negligible vapor pressure. As a liquid approaches its critical point, its properties such as surface tension might change significantly. EMIIm would likely exhibit measurable changes in surface tension as it came closer to phase change, however that transition state (note the critical temperature of EMIIm, See Table 1) would require higher temperatures and lower pressures than this experiment could accommodate.

Equilibrium Droplets and Chemical Reaction

The first series of contact angle measurements involved dispensing a single droplet of EMIIm from a short height (approximately 3 mm) above the substrate. When fully formed (typically with a volume of slightly more than $2\text{ }\mu\text{L}$) the droplet would detach from the needle tip and fall to the substrate, wetting it. This data was taken under ambient temperature and pressure conditions, and was recorded for roughly one hour at a frame rate of $\frac{1}{2}\text{ Hz}$. A sample data set for contact angles recorded on undoped silicon substrate are shown in Figure 8.

It was immediately noticed that the contact angle did not immediately stabilize to a single value, but appeared to decay as a function of time. As the droplet initially struck the surface it would form an angle and then slowly settle and spread to lower angles following a power law relationship. Almost all of the substrates tested except PTFE Teflon exhibited this behavior. This was recognized as the effects described by researchers Kwok and Murmur, described using Equation 3, indicating a chemical reaction.¹⁷²⁰ A curve fitting algorithm was applied using Matlab to obtain power law coefficient values for K and n from the data. The resulting curve fit line and coefficients are shown overlayed with the measured data in Figure 8. The causes of this chemical reaction are complex, however it was suggested by Dr. Dean R. Massey that the reaction may be occurring between the EMIIm and an oxide layer formed by many compounds. The oxide itself may be the source of the reaction, or microscopic surface imperfections due to an oxide layer may trap

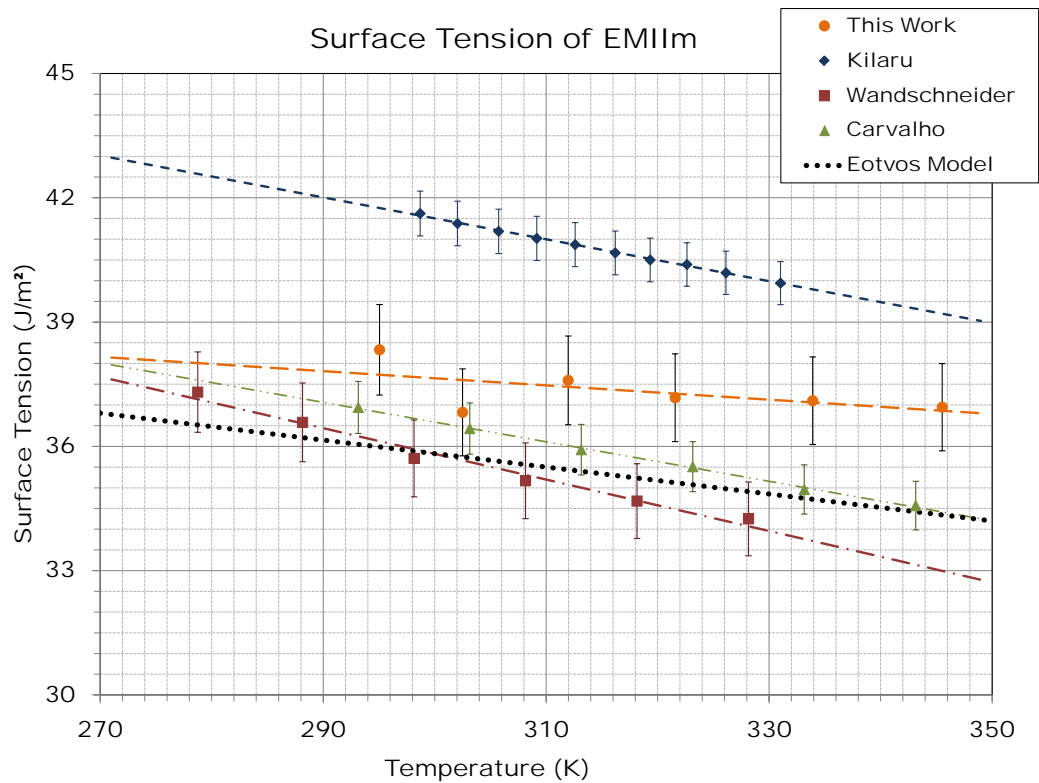


Fig. 6 Graph of EMIIIm Surface tension as a function of temperature from this work, the Eotvos model and other researchers.

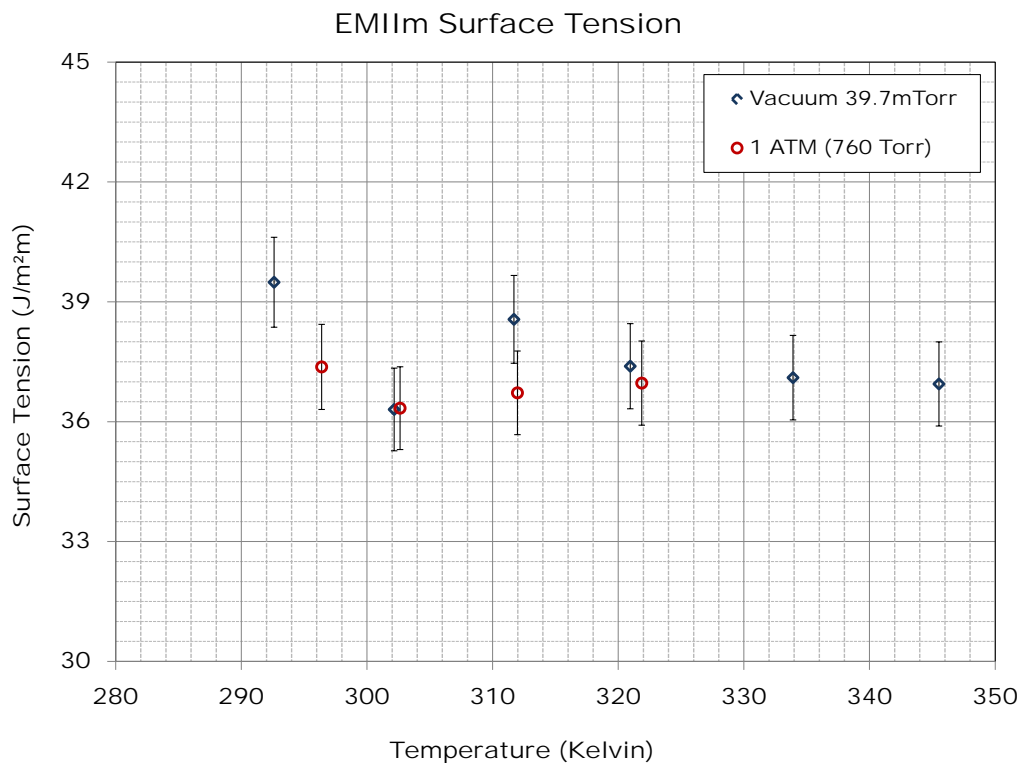


Fig. 7 EMIIIm surface tension as a function of temperature at two different pressures.

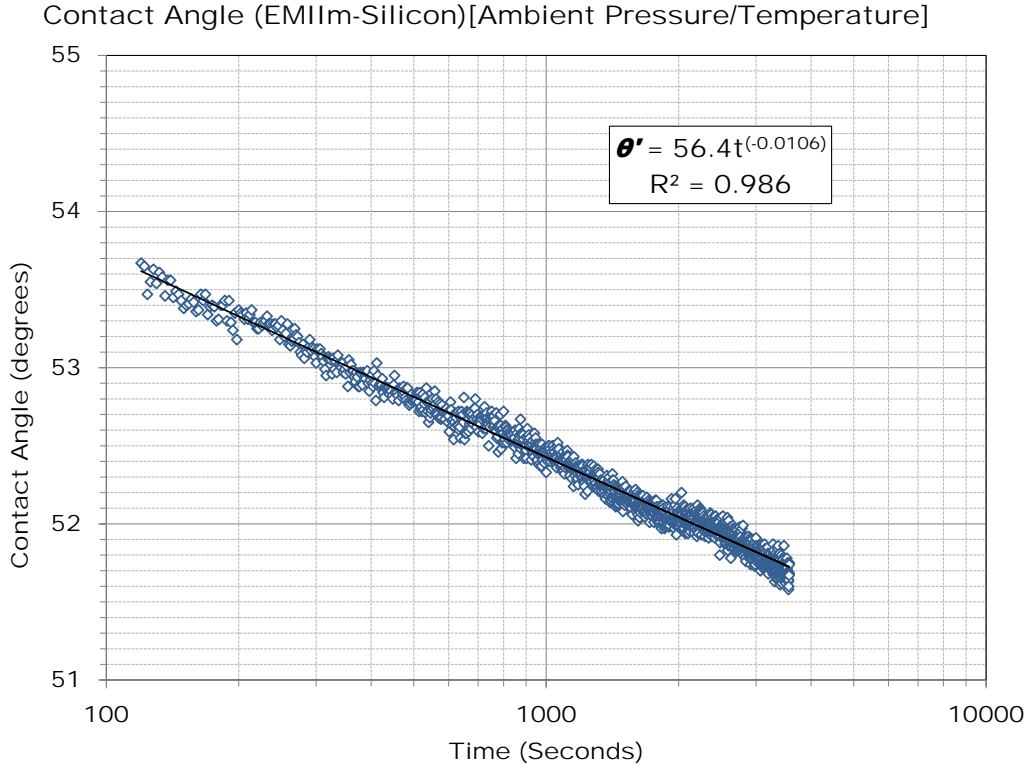


Fig. 8 One hour test on Si, ambient conditions.

Table 3 Coefficients calculated for each EMIIIm/Substrate contact angle profile.

Substrate	k	n	R^2
Fused Silica	57.9	-0.0281	0.99
Soda Lime Glass	45.6	-0.0014	0.71
Kapton	59.3	-0.0079	0.95
Pyrex	45.8	-0.0336	0.94
Annealed Titanium	63.2	-0.0547	0.98
Unsintered Tungsten	39.1	-0.0015	0.44
Undoped Silicon	56.4	-0.0106	0.99
Stainless Steel 316 R_a 0.6	57.2	-0.0055	0.95
Stainless Steel 316 R_a 1.2	60.9	-0.0104	0.72
Stainless Steel 316 R_a 2.5	55.1	-0.0285	0.99
	m	b	R^2
PTFE Teflon	$2 \cdot 10^5$	75.87	0.873

contaminants that are not easily removed. An interesting feature of this data was a change near 120 seconds, when the decay of the droplet angle appears to transition from one power law function to another. The first two minutes of wetting contact came to be viewed as a transient period and were excluded from analysis. This test was carried out for each substrate and the resulting coefficients and figures of merit are shown in Table 3.

These data sets show a wide range of initial wetting angles, k , and rate of spreading terms n . In theory k , the initial ($t = 1s$) contact angle, should be inversely related to the surface energy of the solid γ_s as we showed previously. This behavior is demonstrated in some cases, such as glass exhibiting a much lower k

value than Teflon. Basic soda lime glass has a surface energy over three times greater than Teflon, which is why glass is so easily wetted while Teflon is not. However much of the data did not follow this theory, for instance the tungsten substrate had the lowest k value even though most metals exhibit mid-range surface energy. This is likely due to contamination, vibration or other adverse effects. It can also be seen that k values for the three stainless steel 316 substrates of differing roughness did not form a trend with respect to k . However they did trend with respect to the spreading term n . This trend indicated that increased surface roughness corresponded with a decrease in n , implying a faster rate of wetting/spreading. This agrees with the theory concerning surface roughness and wetting previously discussed.

PTFE Behavior

The only substrate to not follow the power law trend was PTFE Teflon. Teflon produced extremely flat/linear contact angle profiles that converged to a single equilibrium value immediately. Coefficients referred to in Table 3, m and b , are the corresponding coefficients of a linear curve fit. This behavior was not the only way in which Teflon stood out among the substrates tested. Teflon tended to develop an electrostatic charge. The EMIIIm droplets were influenced by this charge and would behave oddly in close proximity. This behavior first manifested as EMIIIm formed a pendant drop at the needle tip. The EMIIIm could be attracted by the charged substrate surface

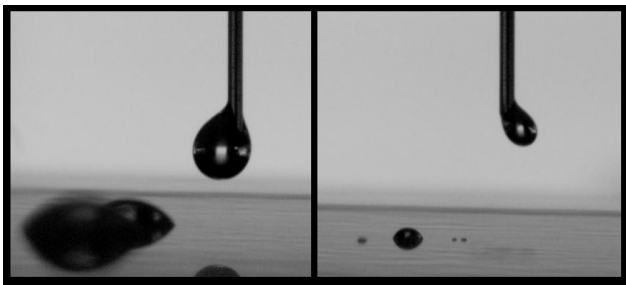


Fig. 9 Sessile droplets behaving strangely during droplet formation due PTFE surface charge.

and discharge too soon, forming extremely small sessile droplets too small to measure. The EMIIIm was also occasionally repelled by the substrate, distorting the pendant droplet as it formed. When finally dispensed the repelled droplet would sometimes fly sideways, out of view, attracted away by an oppositely charged region. A droplet captured in the act of repelled distortion is shown in Figure 9. Once dispensed the droplets were likely to slide between regions of opposed charge and shift out of focus. A few such drops are seen in Figure 9. No effective countermeasure was found for this behavior and data was taken when surface charge of the Teflon happened to be neutral enough to dispense droplets normally.

Equilibrium Droplets and Temperature

It was noticed during testing that if the ambient temperature of the experiment changed in the middle of a test due to lab air conditioning or other causes, the contact angle would also show a slight change. An effort was then made to characterize this behavior. Though too small a difference to measure between consecutive droplets dispensed at different temperatures, it was measurable on a single droplet undergoing temperature change. Testing was then carried out by dispensing a single droplet and allowing it to rest on the substrate for 2 hours. Substrate temperature was then ramped and contact angle data recorded. The most striking response from these tests is shown in Figure 10. We can see that as the temperature of the glass substrate was repeatedly ramped from 280K to 327K, the contact angle oscillated approximately 2 degrees. This can be attributed to changes in the surface tension of EMIIIm with variation in temperature. If we use Equation 1 to calculate the relative change in γ_l as a function of θ (assuming π_{sl} to be constant) we see that a 2 degree shift in contact angle should correspond to a $1.4 \text{ (mN} \bullet \text{m}^{-1}\text{)}$ shift in surface tension. Using the Eotvos model shown in Figure 6 we see that the idealized shift for the same temperature change is approximately $1.5 \text{ (mN} \bullet \text{m}^{-1}\text{)}$, showing close agreement with our measurement.

Advancing & Receding Contact Angles

The final data sets taken were advancing and receding contact angles for each substrate. As previously

described, advancing values should be closest to the ideal contact angle θ , and H should be 0 for an ideal system. Testing revealed that the only data set that appeared close to ideal was Teflon, which exhibited both constant advancing and receding angles. This can be seen in Figure 12. A more representative data set is shown Figure 11, taken on fused silica. Droplet volume/diameter increases and the contact angle stabilizes to a single value. When retracting fluid most of the substrates demonstrated significant adhesion tension. Instead of receding cleanly, the droplet adhered to the surface, approaching a contact angle of zero degrees. This is likely due to surface heterogeneity of the substrates, or due to chemical reaction. Advancing and receding values for each substrate are listed in Table 4.

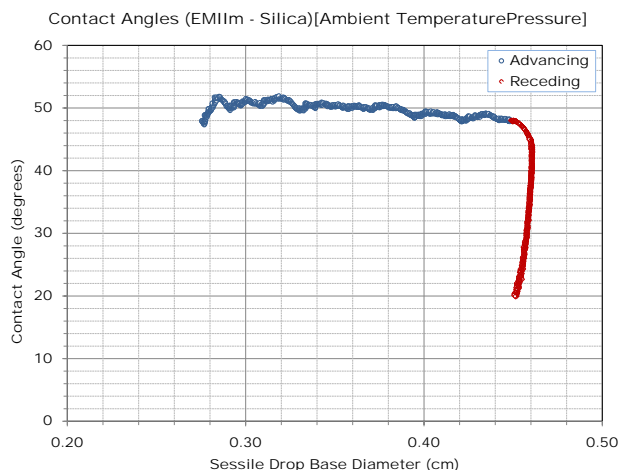


Fig. 11 Advancing and receding contact angles taken on fused silica, as a function of droplet base diameter.

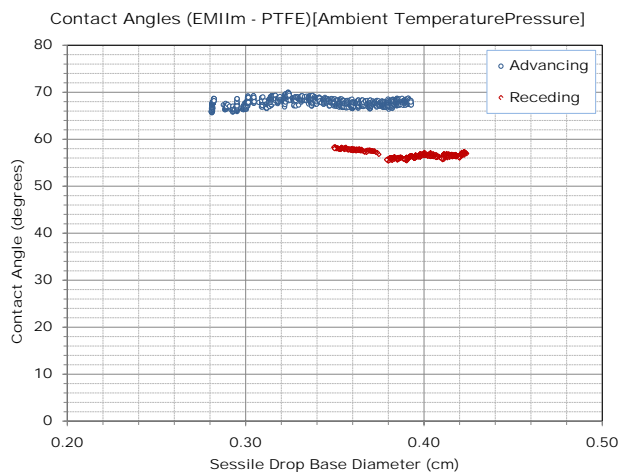


Fig. 12 Advancing and receding contact angles taken on Teflon.

Summary and Conclusions

A large amount of wetting data was taken for each substrate with respect to EMIIIm, materials and different operating conditions. Though these measure-

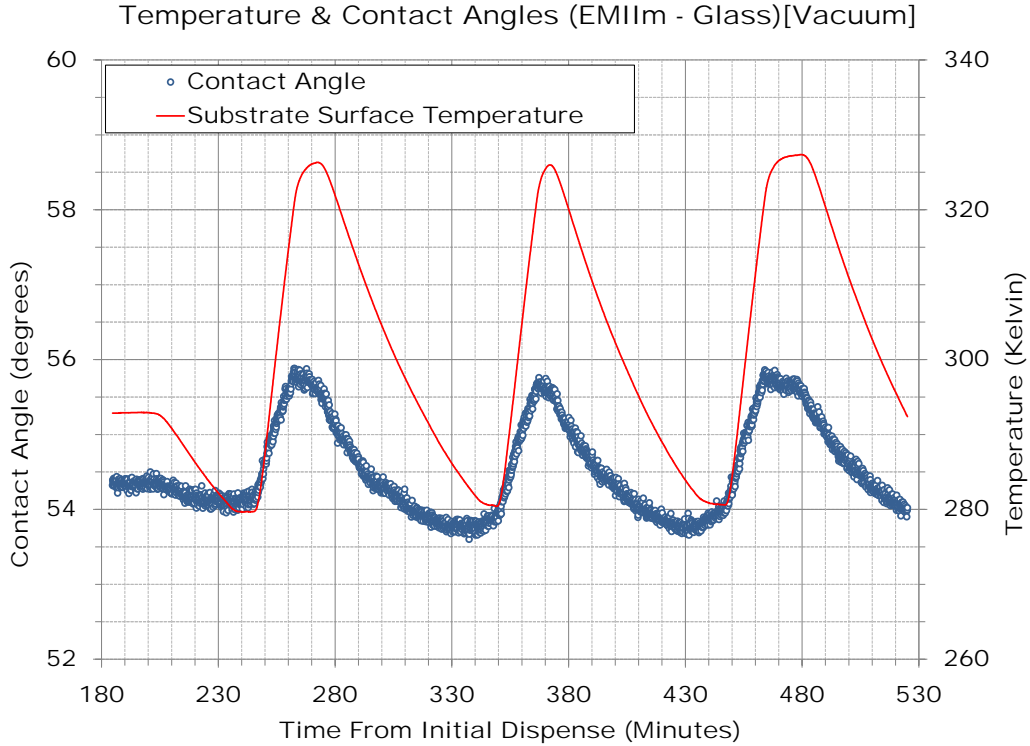


Fig. 10 Change in contact angle and temperature on glass.

Table 4 Advancing and receding angles measured for each substrate.

Substrate	θ_A	θ_R
Fused Silica	51.6	0
Soda Lime Glass	55.2	0
Kapton	52.3	0
Pyrex	49.6	0
Annealed Titanium	52.3	0
Unsintered Tungsten	43.8	0
Undoped Silicon	48.0	0
Stainless Steel 316 R_a 0.63	52.1	0
Stainless Steel 316 R_a 1.2	58.2	0
Stainless Steel 316 R_a 2.5	55.86	0
PTFE Teflon	68.3	56.6

ments exhibit some uncertainties, likely due to surface heterogeneity and contamination, some valuable relationships were observed during this experiment. Chief most among these is the lack of wetting that occurs between EMIIm and PTFE Teflon. Teflon is the one substrate that consistently resisted adhesion with EMIIm. This property of Teflon could have many applications with respect to electrosprays. Selectively coating components such as the chamfer of an internally wetted needle tip with Teflon could help inhibit bubble formation in the propellant and arcing between the extraction grid and emitter. Extraction grids could also be coated with Teflon on the nozzle side to inhibit the spread and accumulation of errant propellant. This could also have the added effect of adding an ex-

tra layer of insulation to prevent arcing.

Techniques to inhibit or promote wetting as desired on a specific substrate were also demonstrated by this research. Surface treatment of stainless steel showed that increased surface roughness affects the rate at which a liquid spreads for certain liquid/solid combinations. This observation could be used to promote wetting for electrospray components propellant wetting or wicking is desirable. Conversely any region where wetting is not wanted should be made as smooth as possible to inhibit droplet adhesion and spread.

Temperature and pressure have also been evaluated with respect to wetting characteristics. It was found that pressure variation has no measurable effect on wetting behavior. Increased temperature has been shown to induce more wetting between EMIIm and most propellants. Likely due to changes in the surface tension of the propellant, this behavior could be used to promote or limit wetting in different regions of the thruster with selective heating/cooling. Expecting EMIIm to easily wet a solid at frigid temperatures typical of the space environment may be a poor assumption.

We have shown that wetting can have a significant effect on electrospray operation and have identified both electrospray failure mechanisms and possible benefits associated with material wetting properties. Wetting behavior due to material, surface treatment and temperature must be taken into account during the materials selection and design phase in order to

improve electrospray reliability.

Future Work

Future work of interest includes testing on EMIIM that has been dessicated to a lower water content using a nitrogen titration process. This would yield EMIIm with a water content comparable to contemporary research ($< 10^3 ppm$), possibly leading to more stable/accurate results. It is also of interest to test a wider array of substrates to broaden the number of materials evaluated for electrospray components. As this paper shows, Teflon is the only substrate that actively resists adhesion with EMIIm. Identifying a non-insulating material or surface treatment with similar wetting properties would be useful. Electrosprays have been proposed as a secondary, high efficiency, μN propulsion system utilizing the same propellant as chemical systems for multi-mode spacecraft propulsion. AF-315 is a hydrazine alternative that is also an ionic liquid suitable for use as electrospray propellant.

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